Report as of FY2010 for 2009MO099B: "Visible Light-activated Titanium Dioxide-based Photocatalysts:"

Publications

- Articles in Refereed Scientific Journals:
    - Hua, B.; Veum, K.; Yang, J.; Jones, J.; Deng, B. (2010) Parallel factor analysis of fluorescence EEM spectra to identify THM precursors in lake waters", Environmental Monitoring and Assessment, 161 (1-4), pp. 71-81.
- Conference Proceedings:
    - Huy Nguyen and Baolin Deng, Nitrogen-Doping of Arrays of Titanium Dioxide Nanotube by Non-Thermal Plasma Processing Technique to Improve Photoatalytic Efficiency in Visible Lights for Environmental Applications , Poster presentation on the Missouri NanoFrontiers Symposium 2010, hosted in the Washington University at St Louis.

Report Follows

Abstract
Titanium dioxide (TiO2) has been widely used as a photocatalyst for the advanced oxidation treatment of organic contaminants and disinfection when coupled with ultraviolet (UV) radiation. Much efforts has recently focused on modifying TiO2 so it can be activated with visible light (VIS), which could result in much broader environmental applications. TiO2 doped with elements such as carbon and nitrogen (N) are found to exhibit photocatalytic effects in VIS region. The efficiency of these modified photocatalysts, however, is still low. The objective of this proposed study was to synthesize and characterize the N-doped TiO2 nanomaterials capable of significant visible light absorption and evaluate their photocatalytic reactivity under visible light radiation for the degradation of petroleum hydrocarbons, such as degradation of petroleum hydrocarbons, disinfection of treated municipal wastewater prior to final discharge to rivers and lakes, and destruction of indoor air pollutants.

TiO_2 nanotubes were prepared from titanium (Ti) foil by the anodic annodization process. This material was then treated by a non-thermal plasma processing technique in nitrogen atmosphere to achieve nitrogen doping. The results showed that TiO_2 as array of nanotubes could be nitrogen-doped with the non-thermal plasma processing technique without noticeable damage to the 1-dimensional structure. Using methylene blue (MB) as a sample organic contaminant, the doped TiO_2 nanotubes showed a clear improvement in photocatalytic efficiency, as well as effective activation with visible lights

Nature, Scope and Objective of Research:

Since the discovery of its photoactivity in 1972 (Fujishima and Honda 1972), titanium dioxide (TiO2) has been widely used as a photocatalyst for disinfection and contaminant degradation (Chen and Mao 2007). However, original TiO2 can only be activated by ultra-violet (UV) radiation due to its high energy band gap. Since less than 10% of the total solar radiation to the earth's surface is in the UV range, photocatalytic processes mediated by TiO2 require an anthropogenic UV source. Much effort has recently been devoted to modifying TiO2 to achieve activation in the visible light region (Asahi et al. 2001). Notably nitrogen (N)-doped TiO2 is found capable of absorbing visible light (Asahi and Morikawa 2007; Chen and Mao 2007). However, applications of N-doped TiO2 nanomaterials in water treatment have not been explored.

The objective of this proposed study was to synthesize and characterize the N-doped TiO2 nanomaterials capable of significant visible light absorption and evaluate their photocatalytic reactivity under visible light radiation for the degradation of petroleum hydrocarbons. This is an integral part of our long-term goal to prepare solid thin-film and nano-structured photocatalysts with a superior quantum yield and explore their environmental applications such as degradation of petroleum hydrocarbons, disinfection of treated municipal wastewater prior to final discharge to rivers and lakes, and destruction of indoor air pollutants.

This proposed study was built on mature TiO_2/UV processes that have been widely used for disinfection and advanced oxidation of organic contaminants. The result from this study could extend the photocatalytic treatment processes to visible light region, avoiding the need for an UV source. Degradation of petroleum hydrocarbons was selected as the first model system for application because oil spills occur frequently; and it was envisioned that if an effective photocatalyst could be prepared that utilizes visible light radiation, application of the catalyst to the contamination sites could be a new and economical approach of contamination degradation.

Another application was for the treatment of produced water associated with gas and oil production. Dissolved aromatics hydrocarbons in the produced water include benzene, toluene, ethyl benzene and xylene (BTEX), which are potent carcinogens. Currently, produced water is mainly treated with physical treatment techniques such as filtration, gravity separation and flotation. These techniques are expensive and not able to treat the water to meet standards for reuse. Drinking water standards are even more rigid, which are 0.005, 1, 0.7, and 10 ppm for benzene, toluene, ethyl benze ne and xylene, respectively (http://www.epa.gov/safewater/contaminants/index.html#listmcl). The proposed research could potentially provide a cost-effective approach for the produced water treatment and reuse.

Synthesis and characterization of VIS-activated N-doped TiO_2 photocatalysts

Two approaches were employed to prepare N-doped TiO_2 photocatalyst nanomaterials in this research. The first approach was to prepare a thin solid film of N-doped TiO_2 by the chemical vapor deposition method. In this approach, the N-doped TiO_2 was prepared by atmospheric pressure chemical vapor deposition (APCVD) or plasma enhanced chemical vapor deposition (PECVD). Implementation of APCVD and PECVD was derived from the works of Guo et al. (2007). Precursors including $TiCl_4$, O_2 (as air) and NH_3 gas react at glass substrate surface of 500-600oC for 1 minute, resulting in deposition of TiO_2 and TiN on a substrate of glass. The glass with deposited layer containing TiO_2 and TiN were then annealed at 500oC in nitrogen atmosphere. Conditions for sample preparation was altered including the reactant concentration and treatment time in order to obtain the best materials with the highest catalytic activity. Equipment for chemical vapor deposition and plasma enhanced chemical vapor deposition were available from Professor Hao Li's laboratories in the Department of Mechanical and Airspace Engineering of University of Missouri. The second approach was to prepare nano-structured N-doped TiO_2 following the sol-gel method by hydrolysis of titanium isopropoxide (TIIP) in ammonia solution, as reported in the literature (Yu et al. 2001). TIIP is applied to ammonia solution drop-wisely. The collected sol was aged for 1 hour inside ultrasonic bath, then to be annealed at 500oC in nitrogen atmosphere. It was expected that nanorods of TiO_2 will be achieved. As-prepared samples then can undergo further treatment by plasma with carrier gas of NH_3. The prepared photocatalyst samples from different approaches was characterized by X-ray diffraction spectroscopy (XRD) for crystal structures and sizes - peak positions and magnitudes in XRD spectroscopy provide information on the crystal type (e.g., anatase or rutine) and nanoparticles size, as illustrated by Figure 1. Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM) analyses was used to examine nanostructures or induced layer of TiO2 at the surface of prepared photocatalysts. Light absorption efficiency of the samples was measured by UV-VIS optical absorption analysis. Specific surface area of the prepared samples was determined by BET method using multi-point nitrogen adsorption.

<u>Summary</u>

TiO_2 nanotubes were prepared from titanium (Ti) foil by the anodic annodization process. This material was then treated by a non-thermal plasma processing technique in nitrogen atmosphere to achieve nitrogen doping. The results showed that TiO_2 as array of nanotubes could be nitrogen-doped with the non-thermal plasma processing technique without noticeable damage to the 1-dimensional structure. Using methylene blue (MB) as a sample organic contaminant, the doped TiO_2 nanotubes showed a clear improvement in photocatalytic efficiency, as well as effective activation with visible lights.

Literature Cited

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